

UCRL-100488
PREPRINT

PHASE BEHAVIOR OF PURE AND MIXED SYSTEMS AT HIGH PRESSURE

Francis H. Ree
Lawrence Livermore National Laboratory
University of California
Livermore, CA 94550

This paper was prepared for submittal to the
International Conference on High Pressure Science and Technology
Paderborn, West Germany
July 17-21, 1989

June 1989

Lawrence
Livermore
National
Laboratory

This is a preprint of a paper intended for publication in a journal or proceedings. Since changes may be made before publication, this preprint is made available with the understanding that it will not be cited or reproduced without the permission of the author.

DISCLAIMER

This document was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor the University of California nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial products, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or the University of California, and shall not be used for advertising or product endorsement purposes.

PHASE BEHAVIOR OF PURE AND MIXED SYSTEMS AT HIGH PRESSURE

FRANCIS H. REE

Lawrence Livermore National Laboratory, University of California
Livermore, CA 94550 USA

Our knowledge of intermolecular potentials, equations of state theories, and methods of handling chemical reactions are at a stage where one can perform rigorous calculations on pure and mixture systems at high pressures and temperatures.

KEY WORDS: melting, phase separation, krypton, xenon, N_2 - H_2O mixture

PURE SYSTEMS: Melting Lines of Krypton and Xenon

We have recently developed a perturbation (PT) theory (Kang *et al.*, 1986), which expands the free energy using the hard-sphere reference potential in such a way that only the first-order correction to the Helmholtz free energy is necessary in most cases to yield reliable thermodynamic properties. We have applied the PT to examine the thermodynamic properties of krypton and xenon (Kim *et al.*, 1989). Such a study is timely, since the diamond-anvil-cell (DAC) technology is beginning to supply P-V data close to 200 GPa, and since Aziz and Slaman (AS) (1986a,b) have constructed very reliable pair and induced multipole potentials. Comparisons of computed results with experimental data shed a light on how condensed phase interactions differ from that of an isolated pair interaction.

Melting properties are sensitive to a small difference in the Gibbs free energies of the fluid and solid phases. The PT permits the computation of solid and fluid phase properties within a single theoretical framework. This is a *unique and essential* feature for calculating melting properties. We computed the melting line of xenon using the PT (Fig. 1). Comparisons with experimental data show that the AS potential gives melting pressures that are too low and that the Axilrod-Teller (AT) triple dipole term, which is repulsive, is necessary in bringing together theory and experiment. Namely, the AT interaction serves to stabilize the fluid phase at the expense of the solid phase. Similar results are obtained for krypton.

The AT three-body force is the dominant many-body force within the pressure range in Fig. 1. At higher pressures, a short-range attractive correction $V_{sr}(r)$ to the AS potential is needed. Barker (1987, 1988) introduced a correction term to match experiment to 5 GPa for krypton and to 50 GPa for xenon. Beyond these points, our calculations show that Barker's modified potentials become too stiff, for example, overestimating the pressure (= 123 GPa) of xenon by about 30 GPa at $V = 11 \text{ cm}^3/\text{mol}$ at 298 K. Following Barker, we have introduced an *ad hoc* $V_{sr}(r)$ to the AS potential so that the effective pair potentials (referred to as ASM) with the AT term agree with static compression data to about 200 GPa for xenon and to 30 GPa for krypton (Kim *et al.*, 1989). The exact nature of $V_{sr}(r)$ is not clear, but it probably originates from the many-body forces

FRANCIS H. REE

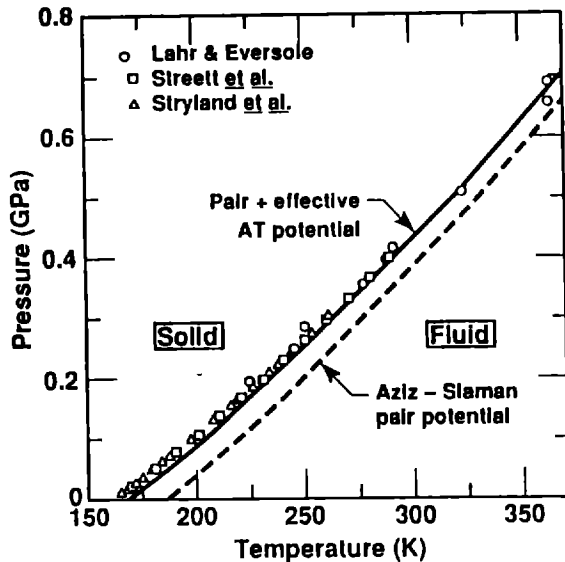


Figure 1. Theoretical and experimental melting lines of xenon. See Kim *et al.* (1989) for experimental references.

associated with the Pauli principle which prevents an overlap of the electron charge density.

A DAC technology at elevated temperatures, which is under various stages of development, will extend melting lines in Fig. 1. According to our best calculations (ASM-AT potential), such an experiment would produce the melting lines which should lie close to those shown in Fig. 2. The melting lines of krypton and xenon approximately follow each other to about 5000 K, but beyond this point the melting pressure of xenon increases faster with temperature. The high-T portion of the melting line of krypton may be less reliable, since compression data used to "back-out" $V_{sr}(r)$ are not available.

MIXTURES: Phase separations in N_2 - H_2O Fluid

Our application deals with a gas-gas phase separation in N_2 - H_2O mixtures using a general chemical equilibrium computer code that minimizes the Gibbs free energy with respect to the composition of chemical species (Ree, 1986). Our calculations approximate an average electrostatic attraction in water molecules by a temperature-dependent attractive

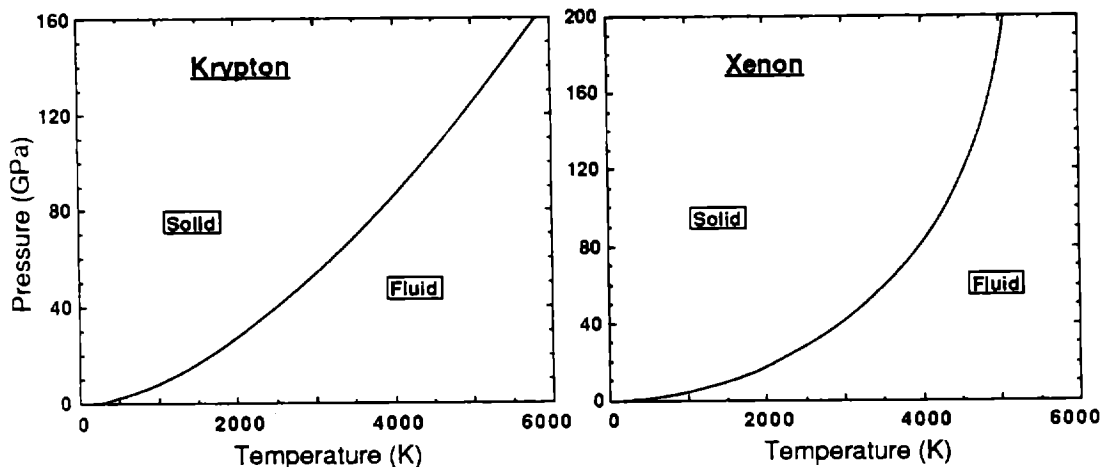


Figure 2. High-temperature melting lines of krypton and xenon as predicted by the PT with the ASM-AT interaction.

PHASE BEHAVIOR OF PURE AND MIXED SYSTEMS AT HIGH PRESSURE

well-depth. The potential parameters are further constrained to agree with shock data for the like-pair interactions and the Lorentz-Berthelot rule for the unlike-pair interaction. Figure 3 shows an isotherm (solid line) for an

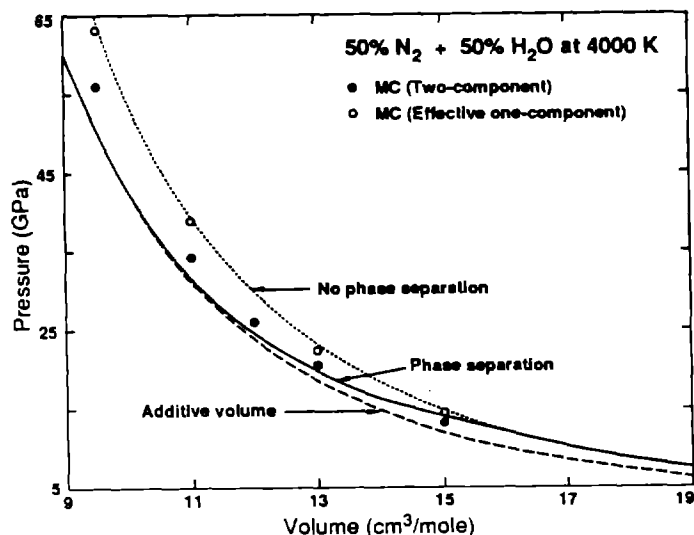


Figure 3. Isotherms of an equimolar N₂-H₂O mixture at 4000 K: comparison between theory/Monte Carlo simulation. See the text.

is shown by open circles (the effective one-component) and the corresponding two-component simulations (which allow a possible demixing of a N₂-rich and a N₂-poor phases) by solid circles. Reasonable agreement between theory and simulation for the two-component calculations reinforces the prediction on the phase separation. Additionally, the first nearest-neighbor peak in the MC N₂-H₂O pair distribution function lies distinctly below those of the like-neighbor pairs. If such a phase separation does indeed occur, it would profoundly affect the detonation behavior of many condensed explosives (Ree, 1986).

Work performed under auspices of U.S. DOE at Lawrence Livermore National Laboratory under contract No. W-7405-ENG-48.

REFERENCES

- Aziz, R. A. and Slaman, M. J., *Mol. Phys.* **58**, 679 (1986); (b) *ibid* **57**, 825 (1986).
- Barker, J. A., *Mol. Phys.* **60**, 887 (1987).
- Barker, J. A., *J. Stat. Phys.* **52**, 1359 (1988).
- Kang, H. S., Ree, T., and Ree, F. H., *J. Chem. Phys.* **84**, 4547 (1986); see references cited therein.
- Kim, J. H., Ree, T., and Ree, F. H., *J. Chem. Phys.*, to be published.
- Ree, F. H., *J. Phys. Chem.* **87**, 2846 (1983).
- Ree, F. H., *J. Chem. Phys.* **84**, 5845 (1986).